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(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).

(72) Inventors: CURTIS, James, Daniel; 432 Dunwoody Court, Blountville, TN 37617 (US). WEINHOLD, Stephen; 3272 Ridgeview Street, Kingsport, TN 37664 (US).

(74) Agents: KATZ, Mitchell, A. et al.; Needle & Rosenberg, P.C., The Candler Building, Suite 1200, 127 Peachtree Street, N.E., Atlanta, GA 30303-1811 (US).

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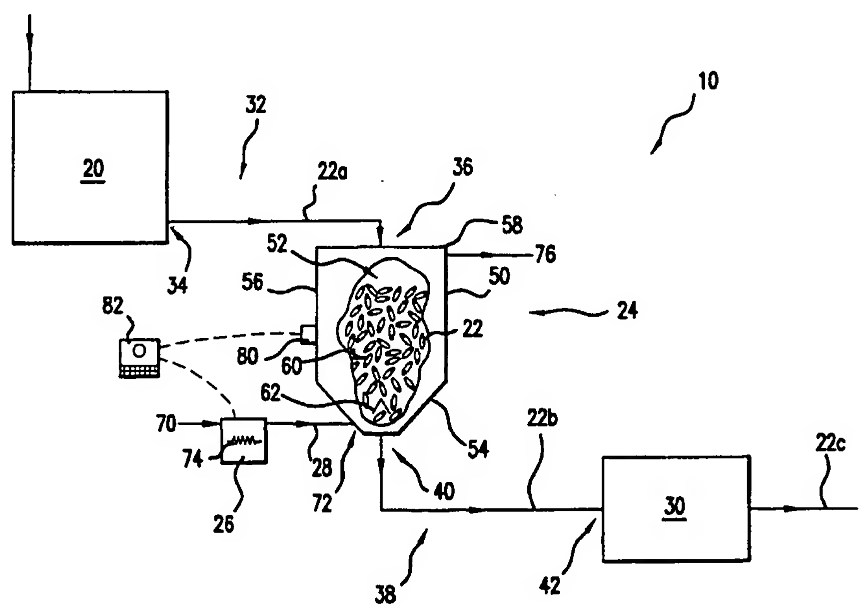


(57) Abstract

A method and apparatus for increasing the crystallization rate of polyethylene terephthalate (PET) articles. Moisture is introduced into the amorphous material to be crystallized by passing the articles through a humidified hopper installed in a processing line after molding and before crystallizing. The hopper provides temperature and humidity control, and is sized to result in a residence time sufficient to impart a predetermined moisture content to surface portions of articles passing therethrough.

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# METHOD AND APPARATUS FOR INCREASING THE RATE OF CRYSTALLIZATION OF THERMOPLASTIC ARTICLES

## Cross-Reference to Related Application

This application claims the benefit of United States Provisional Patent Application Serial No. 60/086,977, filed May 28, 1998.

## Background of the Invention

### Field of the Invention

The present invention relates generally to the field of forming and processing thermoplastic articles, and more particularly to a method and apparatus for increasing the rate of crystallization of thermoplastic articles by introducing moisture into the amorphous thermoplastic article.

### Description of Related Art

Thermoplastic articles or portions thereof are often treated to modify their material characteristics for improved performance in particular applications. For example, the finishes (i.e., the upper portion typically comprising an opening and threads for engaging a cap) of polyethylene terephthalate (PET) preforms made to be blow molded into heat-set containers are sometimes crystallized by heating the finish of the preform, typically by exposure to infrared (IR) radiation. The purpose of subjecting heat set preforms to this process, known as the Yoshino Process, is to convert the amorphous material in this region of the container to crystalline form, and thereby prevent or reduce distortion of the finish of the heat-set bottle during hot filling.

In the Yoshino Process an injection-molded preform is placed in a carrier which shields the body of the preform against exposure to crystallizing heat, but leaves the finishes exposed. This carrier, containing the preform, is then passed through an oven, where the preform finish is exposed to infrared energy for a sufficient amount of time to allow the finish to crystallize. Several factors effect the rate at which the crystallizing machine can process preforms, including polyester resin properties, oven efficiency, temperature the preform attains in the oven, and time spent in the oven.

Efficiency of a manufacturing facility making preforms to be processed in the Yoshino process would be enhanced by increasing the rate of handling and crystallizing of the preforms. U.S. Patent No. 5,261,545 to Ota, et al. provides background information regarding the Yoshino process.

The efficiencies of other processes for crystallizing thermoplastic articles, including PET articles, such as the SRCF process developed by Sidel, can also be enhanced by increased rates of handling and processing.

It has been reported that the rate of crystallization of PET pellets may be increased in portions of the pellets into which moisture has been absorbed. *R. Bianchi, et al., Effect of Moisture on the Crystallization Behavior of PET from the Quenched Amorphous Phase, 43 J. APPL. POLYM. SCI. 1087-89 (1991). Bianchi, et al.*, however, suggest that material behind the humidity front (i.e., "dry" PET) experiences lower crystallization rates, while material ahead of the humidity front (i.e., "wet" PET) experiences higher crystallization rates. Although surface layers readily exposed to moisture may experience increased crystallization rates with brief to moderate absorption periods, according to the teaching of *Bianchi, et al.*, increasing the crystallization rate of inner layers will require prolonged absorption periods in order to permit moisture migration beyond the surface layers. Thus, needs still exists for the provision of increased crystallization rates throughout a PET article without the requirement of prolonged absorption periods.

## Summary of the Invention

In accordance with the purpose(s) of this invention, as embodied and broadly described herein, this invention, in one aspect, relates to a system for processing a plastic article, the system comprising a molding machine for forming a plastic article; an enclosure receiving the plastic article from said molding machine and surrounding at least a portion of the plastic article for exposure to water vapor; and a crystallization machine for receiving the plastic article from said enclosure and crystallizing at least a portion of the plastic article.

In another aspect, the invention comprises an apparatus for introducing moisture into a plastic article, said apparatus comprising a hopper having an article inlet for receiving the plastic article, an article outlet for discharging the plastic article, and an internal volume between said inlet and said outlet; and humidification means for introducing moisture into said internal volume.

In another aspect, the invention comprises a method of crystallizing a plastic article, the method comprising exposing an outer surface of the plastic article to water vapor for a period of time sufficient to increase the moisture content of a surface portion of the plastic; and exposing at least a portion of the moistened plastic article to energy until crystallized.

In another aspect, the invention comprises a method of fabricating a PET container, the method comprising forming an amorphous preform from PET resin, the preform comprising a finish portion and a body portion; exposing at least the finish portion of the preform to water vapor for a period of between about fifteen minutes to six hours; and exposing at least the finish portion of the preform to energy until crystallized.

In another aspect, the invention comprises a method of crystallizing at least a finish portion of a PET container, comprising exposing at least a finish portion of an amorphous container preform to a gas comprising water vapor for a period of between about fifteen minutes to six hours, and exposing at least the finish portion of the preform to energy until crystallized.

In another aspect, the invention comprises an apparatus for the production of heat set containers, comprising a hopper disposed in line between an injection molding machine and a crystallizing machine, said hopper comprising means for circulating warm, moist air.

In another aspect, the invention comprises a method for the production of heat set containers, comprising forming a preform, contacting said preform with a gas comprising water vapor, and crystallizing at least a portion of said preform.

Additional advantages of the invention will be set forth in part in the detailed description, including the drawing figures, which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory of preferred embodiments of the invention, and are not restrictive of the invention, as claimed.

## Brief Description of the Drawing Figures

Figure 1 shows schematically a processing system and apparatus according to a preferred form of the present invention, a hopper portion of the system shown in partial cutaway view.

Figure 2 graphs the effect of absorbed water on the crystallization rate from the glass of amorphous PET stored at different humidities, plotted by temperature.

Figure 3 graphs the effect of absorbed water on the crystallization rate from the glass of amorphous PET stored at different humidities, plotted by the difference between absolute temperature (T) and the glass transition temperature ($T_g$).

Figure 4 graphs the effect of crystallization nucleator additives on the humidity-dependent crystallization halftime from amorphous PET.

Figure 5 graphs the effect of storage humidity on the crystallization halftime from amorphous PET.

Figure 6 graphs the development of crystallinity in a PET article during immersion in a liquid bath after storage at different humidities.

Figure 7 graphs the water concentration profile in an initially dry 0.635 mm thick PET sheet after exposure to humid conditions at 23°C for different periods.

Figure 8 graphs the effect of storage time under humid conditions on the crystallinity developed during immersion in a liquid bath at 130°C for 120 seconds in a 0.635 mm thick PET sheet.

## Detailed Description of Preferred Embodiments

The present invention may be understood more readily by reference to the following detailed description of preferred embodiments of the invention, including the appended drawing figures referred to herein, and the examples provided therein. It is to be understood that this invention is not limited to the specific systems, devices and/or processes and conditions described, as specific systems, devices, processes and/or process conditions for processing plastic articles as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

It must also be noted that, as used in the specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the context clearly dictates otherwise. For example, reference to processing "a plastic article" is intended to include the processing of a plurality of plastic articles or a series of articles. Ranges may be expressed herein as from "about" or "approximately" one particular value and/or to "about"or "approximately" another particular value. When such a range is expressed, another embodiment includes- from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent "about," it will be understood that the particular value forms another embodiment.

Without being bound by the theories of operation set forth herein, it has been discovered that the crystallization rate of amorphous PET can be increased throughout substantially the entire thickness of an article by introducing moisture content into only the surface layers of the article in a controlled manner before processing by a crystallization machine. In particular, and by way of example, significant increases in the efficiency of processing heat-set PET container preforms, PET containers such as formed bottles, PET heating trays, PET sheets, and other PET articles, and/or selected

portions thereof, using the Yoshino process, the SRCF process, or other crystallization processes, may be obtained by means of the method and apparatus described herein.

Briefly described, in one presently preferred aspect, the present invention comprises an apparatus for introducing moisture into plastic articles. The apparatus preferably includes a hopper or other enclosed container having an inlet for receiving plastic articles, an outlet for discharging plastic articles, and an internal volume between the inlet and outlet. The apparatus preferably also is provided with humidification means for introducing moisture into the internal volume. Temperature control means can optionally also be provided for controlling the temperature within the internal volume. The inlet of the hopper can be coupled by a material handling device or conduit in-line to the discharge of an injection molding machine, whereby PET preforms or other plastic articles formed in the injection molding machine are introduced into the hopper. The outlet of the hopper can be coupled by a second material handling device or conduit in-line to the inlet of a crystallization machine, whereby the wetted preforms are discharged from the hopper into the crystallization machine.

In another preferred aspect, the present invention comprises a system for processing plastic articles such as, for example, PET preforms for heat-set containers. The system preferably includes an injection molding machine for forming amorphous plastic articles; a hopper or other enclosure having an article inlet for receiving plastic articles from the injection molding machine, an internal volume for retaining a plurality of plastic articles, a vapor inlet for receiving a gas stream containing water vapor, and an outlet for discharging plastic articles from the internal volume; and a crystallizer for crystallizing at least a portion of each plastic article discharged from the hopper.

In another preferred aspect, the present invention comprises a method of crystallizing plastic articles. The method of the present invention preferably includes the steps of exposing an outer surface of a plastic article to a gas comprising water vapor for a period of time sufficient to increase the moisture content of a surface

portion of the plastic, and heating or otherwise exposing the moistened plastic to energy until crystallized.

In another preferred aspect, the present invention comprises a method of fabricating a PET container. The method comprises first forming an amorphous preform from PET resin, the preform comprising a finish portion and a body portion. At least the finish portion of the preform is exposed to water vapor, preferably by contact with a fluid or other material such as a gas comprising water vapor, for a period of time sufficient to increase the moisture content of a surface portion of at least the finish portion of the preform. At least the finish portion of the preform is exposed to energy until crystallized. Finally, the preform is molded to form a container. In a preferred embodiment, the step of exposing the preform to a gas comprising water vapor is accomplished by introducing a gas comprising water vapor into a hopper and passing a stream of preforms through the hopper. The preform is preferably exposed to the gas comprising water vapor for a period of time between fifteen minutes to six hours, the gas preferably having a temperature between approximately 20°C to 60°C, and a relative humidity of between approximately 20% to 100%.

Referring now to the drawing figures, wherein like reference numerals represent like parts throughout, example and preferred forms of the present invention will now be described. The present invention relates to an improved system, apparatus and method for the production of heat set containers.

As seen best with reference to Fig. 1, in a preferred form, the present invention comprises a system 10 for processing plastic articles, the system 10 generally comprising an injection molding machine 20 or other device for producing a stream of plastic articles 22; a hopper 24 or other enclosure coupled in-line with the injection molding machine 20, humidification means 26 for introducing a gas stream containing water vapor 28 into the hopper 24 or other enclosure; and a crystallization machine 30 coupled in-line with the hopper 24 or other enclosure for further processing the plastic articles 22. The injection molding machine 20 and crystallization machine 30 are well known pieces of equipment which need not be described in detail here. Suitable

injection molding machines 20 are commercially available from Husky, Cincinnati Millicron, and a number of other manufacturers. Crystallization machines 30 are operated in crystallization processes by Yoshino and Schmalbach-Lubeca Plastic Containers U.S.A., and according to the SRCF process developed by Sidel.

In a further preferred form, the system 10 of the present invention comprises first material transfer means 32 for transferring the plastic articles 22 from a discharge 34 of the injection molding machine 20 to an article inlet 36 of the hopper 24. The first material transfer means 32 can take any of a number of forms, including without limitation, conveyor belts, metering devices, shaker tables, screw conveyors, gravity-fed conduits, or any other transfer device as would be readily apparent to one of ordinary skill in the art. The system 10 can further comprise a second material transfer means 38 for transferring the plastic articles 22 from an article discharge 40 of the hopper 24 to an inlet 42 of the crystallization machine 30. The second material transfer means 38 can also take any of a number of forms, including without limitation, conveyor belts, metering devices, shaker tables, screw conveyors, gravity-fed conduits, or any other transfer device, and may take the same form as, or a different form than, the first material transfer means 32.

The hopper 24 of the present invention preferably comprises a housing 50 enclosing an internal volume 52. The housing 50 is preferably formed from sheetmetal, plastic, or other substantially rigid, low-friction, wear-resistant material. At least a lower portion of the housing 50 is preferably provided with one or more inwardly converging, sloped walls 54, to funnel the plastic articles 22 within the internal volume 52 into the article discharge 40. The upper portion of the housing 50 can comprise one or more straight walls 56, and a roof 58, forming a cylindrical or multi-sided enclosure. One or more transparent or translucent portions or sections can be provided in the walls 54, 56 and/or the roof 58, to provide a sightglass or window for external monitoring of the internal volume 52 of the hopper 24. Article flow control means can optionally be provided in and/or adjacent the hopper 24, for controlling the flow of plastic articles through the hopper 24. For example, one or more baffles 60 can be provided for directing articles along a circuitous path through the hopper 24. The baffles 60 can take

the form of, for example, shelves, projections, ribs or bars extending from or between walls of the hopper 24, and/or supported by or from the floor or roof of the hopper 24, or by or from other structures adjacent the hopper 24. Additionally or alternatively, an inverted cone 62, or other article flow control means can be provided above the discharge 40 from the hopper 24. The article flow control means prevent core flow or "rat holing" of individual articles through the hopper 24, thereby promoting plug flow through the hopper 24 and helping ensure that all articles processed through the hopper 24 are exposed to moisture therein for approximately equal residence times. Fluid distribution means can also optionally be provided in or adjacent the hopper 24. The fluid distribution means can comprise the same structures as the article flow control means, such as for example baffles 60 or inverted cone 62, and/or other structures such as screens or fins. The fluid distribution means assists in evenly distributing the moist air through the entire volume of the hopper for contact with articles therein.

The humidification means 26 preferably receives a flow of liquid water 70 from an external source (unshown), converts the liquid water 70 to water vapor, and introduces the water vapor into a material such as a flow of air or other gas. The moist gas 28 is then introduced into the internal volume 52 of the hopper 24 through a vapor inlet 72. In this manner, the hopper 24, as described in greater detail above, and the humidification means couple to form a humidification hopper apparatus for introducing moisture into plastic articles 22 within the internal volume 52 of the hopper 24. The humidification means 26 can accomplish water vaporization in any of a number of ways, including for example, through the use of a resistive heating element for vaporizing water, a combustion-heated vaporizer, ultrasonic vaporization devices, and/or evaporative vaporization surfaces. The humidification means 26 preferably further comprises a temperature control means 74 for controlling the temperature of the moist gas 28 introduced into the hopper 24. The temperature control means 74 can take any of a number of forms, including for example, a resistive heating element, a combustion heater, and/or a heat-transfer element for transferring heat from an external source to the moist gas 28. The temperature control means 74 can be the same element or a different element than is utilized to accomplish water vaporization.

In preferred form, the flow of moist air 28 though the hopper 24 is cross-current (i.e., in a generally opposite direction) to the flow of plastic articles 22 through the hopper 24. Most preferably, the plastic articles 22 are gravity fed through the hopper 24 from an article inlet 36 adjacent the top of the hopper 24 to an article discharge 40 adjacent the bottom of the hopper 24, while the moist air 28 is introduced into the internal volume 52 of the hopper 24 through a vapor inlet adjacent the bottom of the hopper 24 and after transferring some of its moisture to the plastic articles 22 exits though a vent 76 adjacent the top of the hopper 24. A fan, jet or other motive means (unshown) can be provided for directing the flow of moist air from the humidification means 26, through the hopper 24, and out the vent 76. The moisture-stripped gas exiting the vent 76 can be discharged to the atmosphere, or can be recycled back through the humidification means 26.

The system 10 of the present invention can optionally further comprise one or more monitoring means 80 for monitoring the processing of plastic articles 22 within the hopper 24. For example, the monitoring means 80 can comprise one or more sensors, such as a humidity sensor, a temperature sensor, and/or a weight sensor, for monitoring the humidity within the hopper 24, the temperature within the hopper 24, and/or the weight of the hopper and its contents (to monitor moisture absorption), respectively. The rate of article processing, residence time of articles in the hopper 24, flowrate of moist fluid though the hopper 24, and/or other processing parameters can also be monitored by appropriate monitoring means, if desired. The system 10 of the present invention can optionally further comprise control means 82, such as a thermostat, a humidistat, and/or a computer and associated control software, for receiving data from monitoring means 80 and/or externally input data, optionally processing that data, and transmitting instructions to operatively control the humidification means 26, the temperature control means 74, the article throughput rate, the residence time of articles in the hopper 24, the fluid flowrate and/or other process variables. For example, a computer-controlled closed loop control system can receive input data from sensors monitoring process conditions, analyze or process that data, and output instructions to adjust operating parameters of equipment in the system.

Although the system of the present invention has been described herein with reference to a preferred embodiment comprising a humidification hopper, the system of the present invention can comprise other types of humidified enclosures, coupled to humidification means for providing a flow of gas comprising water vapor, and upstream of a crystallization machine within a container processing line. For example, a humidified hood or chamber can be provided surrounding a horizontal, vertical or otherwise oriented portion of a processing line upstream of the crystallization machine. A portion of a conveyor belt or other means for transferring articles from an injection molding machine to a crystallization machine can pass through the humidified enclosure. The desired residence time can be achieved by appropriate selection of the size of the enclosure, and/or by providing the article transfer means with a more or less circuitous path through the enclosure. The enclosure may be adapted to entirely surround one or more of the plastic articles being processed, having an article inlet for receiving plastic articles and an article discharge for discharging moistened articles. The enclosure may alternatively be adapted to surround only selected portions of one or more of the plastic articles being processed, for example, taking the form of a hood overlying the finish portions of container preforms transported along a driven conveyor portion of a processing line. According to this example embodiment, residence time can be controlled by appropriate selection of a serpentine conveyor path under the hood. Further alternate embodiments of the present invention introduce moisture into the material to be crystallized by exposure to liquid water. For example, one or more thermoplastic articles can be introduced into contact with liquid water in a water bath maintained at temperatures and for durations as disclosed herein with regard to exposure to a gas containing water vapor. Prior to crystallization, any residual liquid water will be removed from the material surface.

The present invention enables increased rates of article throughput in processes for crystallizing plastic articles. The method of the present invention generally comprises exposing a surface of a plastic article to water for a period of time sufficient to increase the moisture content of at least a surface portion of the plastic, and heating or otherwise exposing at least a portion of the moistened plastic article to energy until

crystallized. The step of exposing a surface of a plastic article to water preferably comprises contacting the article with a gas comprising water vapor. The term "surface portion" is intended to refer to those portions of an article extending from an exposed surface of the article into the material forming the article to a depth not extending through the material's entire thickness.

In preferred form, plastic articles 22, such as amorphous PET preforms for containers, containers, trays, or sheets are collected in the internal volume of a hopper 24, preferably substantially as described above, and exposed to warm, moist air 28 generated by humidification means 26 preferably as also described above. "Dry" plastic articles 22a are preferably introduced into an article inlet 36 of the hopper 24 from an injection molding machine 20 coupled in-line with the hopper 24. Moistened plastic articles 22b are preferably discharged from an article discharge 40 of the hopper 24 to a crystallization machine 30 coupled in-line with the hopper 24. The plastic articles 22 are preferably heated in the crystallization machine by exposure to infrared energy, to produce crystallized plastic articles 22c.

The air circulated through the hopper 24 is preferably below the glass transition temperature of PET (approximately 80°C), so that the articles do not distort in shape in the hopper 24. Alternatively, articles can be exposed to air at or above the glass transition temperature of PET for sufficiently brief periods of time so as not to cause distortion of the articles. The air circulated through the hopper 24 should have as high relative humidity as possible without water droplets condensing on the articles upon discharge from the hopper 24. In preferred form, the relative humidity of the air circulated through the hopper 24 is between about 20% to 100%, and most preferably between about 50% to 95%. In preferred form, the moist air circulated through the hopper 24 has a temperature of between about 20°C and about 75°C, more preferably between about 40°C and about 60°C, and most preferably between about 45°C and about 55°C.

The hopper 24 is preferably sized to provide an internal volume 52 of sufficient capacity to result in a residence time within the hopper whereby the moisture content of

outer surface layers of the plastic articles is increased. Thus, the hopper size is linked to the processing rate of the system, the temperature and relative humidity within the hopper, the type of plastic resin being processed, the size of the articles being processed, and the desired residence time within the hopper. Typical preform sizes range between about 35g to 100g or more. Generally, suitable residence times include from about fifteen minutes to about six hours. Within this range, residence times of between about one-half hour to about four hours, and between about one to about four hours, have been found to provide acceptable and efficient results, depending on temperature/humidity conditions selected. Typical system processing rates are in the approximate range of 100-130 articles per minute. Thus, in example embodiments, the hopper 24 will be sized to accommodate between 1,500-30,000, and preferably 6,000-30,000 articles, within its internal volume 52. By measurement of the volume occupied by samples of the particular articles to be processed, the necessary hopper volume required to accommodate the desired quantity of articles can be readily calculated. The temperature, relative humidity, article size and hopper size (i.e., residence time) are mutually interdependent, and can be varied to suit the particular application in view of the disclosure provided herein.

Although the humidification hopper described herein has been found to provide acceptable results, the method of the present invention also can be practiced using other types of enclosures coupled to humidification means providing a flow of gas comprising water vapor. For example, plastic articles can be passed through a humidified hood or chamber surrounding a portion of a processing line upstream of the crystallization machine. The desired residence time can be achieved by appropriate selection of the size of the enclosure and/or the path of the articles therethrough. The enclosure may be adapted to entirely surround one or more of the plastic articles being processed, or to surround selected portions of one or more of the plastic articles being processed. For example, the enclosure may take the form of a hood overlying the finish portions of container preforms. One or more sheets comprising PET can be processed by humidification of at least portions of one or more surface layers thereof, for

example, by passing the sheet(s) or portions thereof adjacent a humidification element such as a hood, table, chamber, vent, or other source of water vapor.

Processing plastic articles according to the method of the present invention increases the moisture content of the surface portions of the articles to an extent sufficient to accelerate the crystallization process. Even though the increased moisture content is preferably limited to the surface portions of the articles, it has been found, as detailed below, that the rate of crystallization is increased throughout the entire thickness of the article. Thus, the present invention obviates the need for prolonged absorption times required to introduce moisture through the entire thickness of an article, as would have been previously expected necessary to take advantage of moisture-induced crystallization rate enhancement. For general background information regarding effects of absorbed water on PET, attention is directed to *R. Bianchi, et al., Effect of Moisture on the Crystallization Behavior of PET from the Quenched Amorphous Phase, 43 J. APPL. POLYM. SCI. 1087-89 (1991)*; and *Stephen Weinhold, Ph.D., The Effect of Absorbed Water on the Crystallization Rate of PET from the Glass, POLYESTER '97 WORLD CONGRESS (November 1997)*, each of which are incorporated by reference herein in their entireties.

The overall rate of crystallization in PET is affected by the crystal growth rate, and the density of crystallization nuclei. The crystal growth rate is simply the rate at which an existing crystal grows. It is influenced by material variables such as composition, microstructural regularity, and molecular weight, and by external variables such as temperature. In thermal crystallization (as opposed to strain-induced crystallization), the nucleation of crystals is primarily heterogeneous. That is, the initial seed crystal forms at the surface of a pre-existing foreign particle in the resin. These particles may be almost anything: catalyst, dust, or a component intentionally added to promote nucleation. The density of crystal nucleation is controlled by the density of these foreign particles as well as the rate at which seed crystals of polymer form at the surface of the particles, which is in turn influenced by material variables and temperature.

The addition of a plasticizer also increases the crystallization rate from the glass by increasing the segmental mobility of the polymer. It is the value of $T-T_g$ that determines this behavior. The presence of the plasticizer increases both the crystal growth rate and the formation of seed crystals on heterogeneous nuclei. Thus, it is to be expected that absorbed water, being a potent plasticizer of PET, will speed the crystallization rate of amorphous PET resin from the glass by increasing both the crystal growth rate and the nucleation density.

The following examples and experimental results are included to provide those of ordinary skill in the art with a complete disclosure and description of particular manners in which the present invention can be practiced and evaluated, and are intended to be purely exemplary of the invention and are not intended to limit the scope of what the inventors regard as their invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.); however, some errors and deviations may have occurred. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric.

Figure 2 shows experimental results demonstrating the crystallization halftime of PET from the glass, determined using differential scanning calorimetry (DSC) at a series of temperatures, for amorphous PET which had been stored at different humidities. Unless specified otherwise, the results graphed in the figures refer to Eastapak PET Copolyester 9921w, manufactured by Eastman Chemical Company of Kingsport, Tennessee. The shorter the halftime, the faster the crystallization rate. Dry PET crystallizes very slowly at the lower temperatures. PET containing some absorbed water crystallizes much faster at the lower temperatures. There is relatively little difference between the crystallization rates of the samples stored at 50% and 100% RH, but a large difference between the dry samples and those stored at the intermediate humidity. Clearly, the first small quantity of water to absorb into PET accelerates its crystallization rate significantly, and additional absorbed water increases the crystallization rate only incrementally.

This result is further demonstrated with reference to Figure 3. This figure shows the same experimental data as depicted in Fig. 2, but plotted against $T-T_g$ instead of the absolute temperature. (The $T_g$ assumed for the wet samples was slightly adjusted to account for the escape of a minor portion of the absorbed water at the crystallization temperature from the unsealed DSC pans used for this work.) The points for all of the wet samples fall on the substantially same curve, indicating that the $T_g$ depression caused by the absorbed water fully accounts for the differences in the crystallization rate of the moderately to very wet samples. However, the curve for the dry PET remains substantially separate. This suggests that some crystallization rate enhancing mechanism other than $T_g$ depression becomes operative at low levels of absorbed water. At higher levels of absorbed water, this mechanism remains in force, and the effects of $T_g$ depression are added to it.

The results shown in the next two figures indicate that this additional rate enhancing mechanism is crystal nucleation. Figure 4 shows the crystallization halftime from the glass at 130°C for three samples of Eastapak CPET Polyester 12822 stored at 0%, 53%, and 100% RH: neat PET and the same resin containing two different crystallization nucleator additives. As expected, increasing the storage humidity from 0% to 53% RH greatly speeds the crystallization rate of the neat resin. Further addition of water causes the modest increase in crystallization rate expected as a consequence of $T_g$ depression. On the other hand, the resins containing the nucleator additives crystallize quite rapidly even when dry. For these samples, absorbed water modestly increases the crystallization rate by the degree expected due to $T_g$ depression over the entire range of storage humidities. The dramatic acceleration of crystallization in going from dry to not-dry is lacking, likely because the factor that the first bit of absorbed water creates in the neat resin – dense crystallization nuclei – is already present in the samples containing the nucleator additives.

Figure 5 shows that only a very low level of absorbed water is required to fully activate the nucleation mechanism. Increasing the storage humidity from 0% to 7% RH reduces the crystallization halftime by a factor of five as a consequence of dense

nucleation. Increasing the storage humidity further adds the more modest effect of $T_g$ depression to the nucleation effect.

Figure 6 shows experimental results using a different crystallization technique. Large pieces of 0.6 mm PET film stored at different humidities were immersed in a liquid bath for different periods, then quenched into ice water. The crystallinity was determined from the measured density of the samples. The results of this experiment are consistent with the DSC investigations: the dry PET crystallized very slowly, while all of the wet samples crystallized much more quickly. In fact, within experimental error, the films stored at 12% RH crystallized just as rapidly as those stored at higher humidities.

Thus, it has been discovered that absorbed water, even at very low concentrations, dramatically accelerates the crystallization rate of PET from the glass. However, the decisive factor in determining whether this effect is useful in commercial package manufacturing processes is how long the PET article must be exposed to moisture. In general, the longer the required exposure time to achieve accelerated crystallization, the less commercially attractive is the process. Figure 7 shows how slowly water diffuses into PET at room temperature. It shows the calculated water concentration profile in a 0.635 mm thick sheet of initially dry amorphous PET after exposure to humid conditions for different periods. Only the outer skins of the sheet contain any water at all after 0.3 hours of exposure, and the central 75% of the sheet remains completely dry. After 1.3 hours, nearly half of the sheet contains no water at all. Even after an exposure time of 8 hours, only a very low concentration of absorbed water exists at the center of the sheet. Thus, only the surface portions of the sheet are provided an increased moisture content in commercially acceptable exposure periods. The slow rate of water diffusion becomes even more problematical for thicker articles: approximately 80 hours are required for any water at all to reach the center of a 2.5 mm thick article, for example.

It has been discovered, however, that although water diffuses slowly into PET at room temperature, the diffusion coefficient of water through PET is greatly accelerated

at typical crystallization temperatures. When an initially dry PET article, exposed to humidity briefly at room temperature to create wet surface layers, is heated to a typical crystallization temperature, the water in the surface layers is free to diffuse very quickly. Some of that water diffuses to the surface and escapes. However, the remaining water diffuses in the opposite direction, into the dry core of the article. Furthermore, since only a very low absorbed water concentration is required to fully activate the crystal nucleation phenomenon, most of the rate enhancing effect of absorbed water is achieved throughout the article.

This is depicted in Figure 8. Initially dry 0.635 mm amorphous PET sheet was exposed to different humidity levels for varying periods ranging from 0.3 to 72 hours, then immersed in a liquid bath at 130°C for 120 seconds. After quenching, the crystallinity of the samples was determined from density. Even a brief, 0.3 hour exposure to humidity significantly increased the level of crystallinity developed. At the higher exposure humidities, 1.3 hours of humidity treatment was sufficient for the full water-enhancement effect to be realized. These samples developed the same degree of crystallinity as those exposed to humidity for longer periods, although the central half of the sheet was completely dry at the moment it was plunged into the hot bath. Thus, in practicing the present invention, a humidification hopper sized to provide a residence time of 1-4 hours is typically sufficient to result in substantially accelerated crystallization rates for a wide array of thermoplastic articles.

Suitable polyesters for the process of the present invention include crystallizable polyester homopolymer or copolymer that are suitable for use in packaging, and particularly food packaging. The present invention provides accelerated crystallization rates for PET resins including those containing an antimony catalyst. Suitable polyesters are generally known in the art and may be formed from aromatic dicarboxylic acids, esters of dicarboxylic acids, anhydrides of dicarboxylic esters, glycols, and mixtures thereof. More preferably the polyesters are formed from repeat units comprising terephthalic acid, dimethyl terephthalate, isophthalic acid, dimethyl isophthalate, dimethyl-2,6-naphthalenedicarboxylate, 2,6-naphthalenedicarboxylic acid,

ethylene glycol, diethylene glycol, 1,4-cyclohexane-dimethanol, 1,4-butanediol, and mixtures thereof.

The dicarboxylic acid component of the polyester may optionally be modified with one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid are: phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, mixtures thereof and the like. Preferably the amount of said second dicarboxylic acid is less than 30 mole% and more preferably less than about 15 mole%.

In addition, the glycol component may optionally be modified with one or more different glycols other than ethylene glycol. Such additional glycols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such glycols include: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane, mixtures thereof and the like. Polyesters may be prepared from two or more of the above glycols. Preferably the amount of said second glycol is less than 30 mole% and more preferably less than about 15 mole%.

The resin may also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, trimethylolpropane, pyromellitic dianhydride, pentaerythritol, and other polyester forming polyacids or polyols generally known in the art.

Also, although not required, additives normally used in polyesters may be used if desired. Such additives include colorants, pigments, carbon black, glass fibers, fillers, impact modifiers, antioxidants, stabilizers, flame retardants, crystallization aids, reheat rate enhancing aids, acetaldehyde reducing compounds and the like.

**Example: Production of Heat-Set PET Containers**

The system, apparatus and method of the present invention are particularly suited for use in the production of heat-set PET containers. A PET preform is molded in the injection molding machine 20 from a PET resin. The preform is molded according to known techniques, whereby polyester pellets are dried and injection molded to produce clear, amorphous polyester preforms. The amorphous or "glassy" preforms preferably comprise a threaded finish portion and a body portion. The finish portion is crystallized according to the present invention to prevent distortion of the finish upon further processing of the preform to produce a container, or upon heat-filling of the container. The body portion of the preform is typically processed, as by heated blow molding, to form a container having a desired shape and size.

Directly after forming the preforms, the preform is transported through a hopper substantially as described above. The preforms exit the injection molding machine and are collected in the hopper, where the preforms are contacted with a gas comprising water vapor for a period of time sufficient to increase the moisture content of the internal and external surface portions of the preform. For example, moisture is preferably introduced to surface portions of at least about 5%, or alternatively, at least about 10%, of the total thickness of the preform finish, on both the internal and external surfaces of the preform, thereby introducing moisture to about 10%, or alternatively, about 20%, respectively, of the total thickness of the preform finish.

As the preforms leave the hopper, they are transported directly to a crystallization machine. The preforms are preferably loaded into carriers which shield the bodies of the preforms against exposure to crystallizing heat, but leave the finishes exposed. The carriers, containing the preforms, are then passed through the crystallizing machine, where the preform finishes are exposed to infrared energy for a

sufficient amount of time to allow the finishes to crystallize. This stage preferably involves exposing at least a portion of the preform finish to radiant heat from lamps in a row of ovens (across a spectrum that may include the IR range) while protecting the body of the preform. The finish is heated to temperatures at which the selected polyester crystallizes rapidly (for PET about 150 to about 180°C). This results in a highly crystalline finish. These high levels of crystallinity give dimensional stability to the finish that enable the resulting container to be hot-filled without suffering from thermal distortion in the finish region.

The preforms can then be further processed according to known molding techniques such as blow molding. Excess moisture on the preforms as they are molded degrades the hot fill performance of containers and alters orientation characteristics of the polymer, which are detrimental to heat set containers. Therefore, the moisture content of the preform should be decreased back to conventional levels prior to blow molding the preform. This can be accomplished, for example, by shipping and storing the preforms in standard shipping containers (i.e., unsealed from the atmosphere) and warehousing under ambient conditions, by drying in a dryer, or by other drying means.

The desired container is then formed from the preform and heat-set, according to known techniques. The preform body with the crystallized finish is exposed lamps emitting radiant heat (which may include the IR range of the spectrum) until the preform has reached the appropriate temperature range for bottle blowing (from about 85 to about 120°C for PET). At which time the preform is removed from the oven and placed into a warm or hot blow mold and pressurized. The preform is thereby stretched into a bottle which is held against the warm or hot blow mold (therefore, the name "heat-set"). These bottles are typically designed to withstand hot-filling without shrinkage greater than about 1% by volume and to resist vacuum collapse. It is desirable to achieve a large degree of spherulitic crystallinity in the bottle sidewall in order to resist thermal distortion upon hot-filling of the bottle.

Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference

into this application in order to more fully describe the state of the art to which this invention pertains.

It will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

**What is Claimed is:**

1. A system for processing a plastic article, the system comprising:

   (a) a molding machine for forming a plastic article;

   (b) an enclosure receiving the plastic article from said molding machine and surrounding at least a portion of the plastic article for exposure to water vapor; and

   (c) a crystallization machine for receiving the plastic article from said enclosure and crystallizing at least a portion of the plastic article.

2. The system of Claim 1, wherein the crystallization machine processes the plastic article according to the Yoshino process.

3. The system of Claim 1, wherein the enclosure comprises a hopper having an article inlet for receiving a plastic article from said molding machine, an internal volume for retaining at least one plastic article, a vapor inlet for receiving a gas stream comprising water vapor, and an article discharge for discharging a plastic article from the internal volume.

4. The system of Claim 3, further comprising first material transfer means for transferring a plastic article from a discharge of said molding machine to the article inlet of the hopper.

5. The system of Claim 4, further comprising second material transfer means for transferring a plastic article from the article discharge of said hopper to an inlet of the crystallizer.

6. The system of Claim 3, further comprising a gravity fed conduit for transferring a plastic article from a discharge of said molding machine to the article inlet of the hopper.

7. The system of Claim 3, wherein the vapor inlet is adjacent the article discharge of said hopper, and a vent for discharging the gas stream is adjacent the article

inlet of said hopper, whereby flow of the gas stream through the hopper is generally cross-current to flow of plastic articles through the hopper.

8. The system of Claim 1, further comprising humidification means for generating the water vapor.

9. The system of Claim 8, wherein said humidification means comprises a heating element for vaporizing liquid water.

10. The system of Claim 9, wherein said humidification means comprises temperature control means for controlling the temperature of the gas stream.

11. The system of Claim 10, further comprising monitoring means for monitoring the processing of articles within said enclosure.

12. The system of Claim 11, further comprising control means for operatively controlling the humidification means.

13. An apparatus for introducing moisture into a plastic article, said apparatus comprising:

    (a) a hopper having an article inlet for receiving the plastic article, an article outlet for discharging the plastic article, and an internal volume between said inlet and said outlet; and

    (b) humidification means for introducing moisture into said internal volume.

14. The apparatus of Claim 13, wherein said humidification means comprises a heating element for vaporizing liquid water.

15. The apparatus of Claim 13, wherein said humidification means comprises temperature control means for controlling the temperature within said internal volume.

16. The apparatus of Claim 15, further comprising monitoring means for monitoring the processing of articles within said internal volume.

17. The apparatus of Claim 16, further comprising control means for operatively controlling the humidification means.

18. The apparatus of Claim 13, further comprising article flow control means for controlling the flow of plastic articles through said hopper.

19. The apparatus of Claim 13, further comprising fluid distribution means for controlling the distribution of moisture within said hopper.

20. A method of crystallizing a plastic article, the method comprising:

    (a) exposing a surface of the plastic article to water for a period of time sufficient to increase the moisture content of a surface portion of the plastic article; and

    (b) exposing at least a portion of the moistened plastic article to energy until crystallized.

21. The method of Claim 20, wherein the period of time the plastic article is exposed to water is less than about six hours.

22. The method of Claim 21, wherein the period of time the plastic article is exposed to water is more than about fifteen minutes.

23. The method of Claim 20, wherein the step of exposing a surface of a plastic article to water for a period of time sufficient to increase the moisture content of a surface portion of the plastic, comprises introducing a gas comprising water vapor into a humidification hopper and passing a stream of plastic articles through the humidification hopper at a flowrate.

24. The method of Claim 23, further comprising controlling the flowrate and providing a humidification hopper selectively sized to result in a residence time of individual plastic articles within the humidification hopper of between about fifteen minutes to about six hours.

25. The method of Claim 24, further comprising monitoring the processing of plastic articles within the humidification hopper.

26. The method of Claim 25, further comprising controlling the temperature and humidity of the gas comprising water vapor introduced into the humidification hopper.

27. The method of Claim 23, wherein the temperature of the gas comprising water vapor introduced into the humidification hopper is maintained between about 20°C to about 75°C.

28. The method of Claim 23, wherein the temperature of the gas comprising water vapor introduced into the humidification hopper is maintained between about 40°C to about 60°C.

29. The method of Claim 23, wherein the temperature of the gas comprising water vapor introduced into the humidification hopper is maintained between about 45°C to about 55°C.

30. The method of Claim 23, wherein the relative humidity of the gas comprising water vapor introduced into the humidification hopper is maintained between about 20% to about 100%.

31. The method of Claim 23, wherein the relative humidity of the gas comprising water vapor introduced into the humidification hopper is maintained between about 50% to about 95%.

32. The method of Claim 20, wherein the step of exposing at least a portion of the moistened plastic article to energy until crystallized, comprises heating at least a portion of the moistened plastic article through exposure to radiant energy.

33. The method of Claim 32, wherein the radiant energy is at least partially within the infrared region of the energy spectrum.

34. A method of fabricating a PET container, the method comprising:

(a) forming an amorphous preform from PET resin, the preform comprising a finish portion and a body portion;

(b) exposing at least the finish portion of the preform to a gas comprising water vapor for a period of between about fifteen minutes to about six hours; and

(c) exposing at least the finish portion of the preform to energy until crystallized.

35. The method of Claim 34, further comprising molding the at least partially crystallized preform to form a container.

36. The method of Claim 34, wherein the step of exposing at least the finish portion of the preform to a gas comprising water vapor comprises introducing a gas comprising water vapor into a hopper and passing a stream of preforms through the hopper.

37. The method of Claim 36 wherein the step of exposing at least the finish portion of the preform to a gas comprising water vapor further comprises providing humidification means for generating a flow of gas having a temperature between about 20°C to about 60°C, and a relative humidity of between about 20% to about 100%.

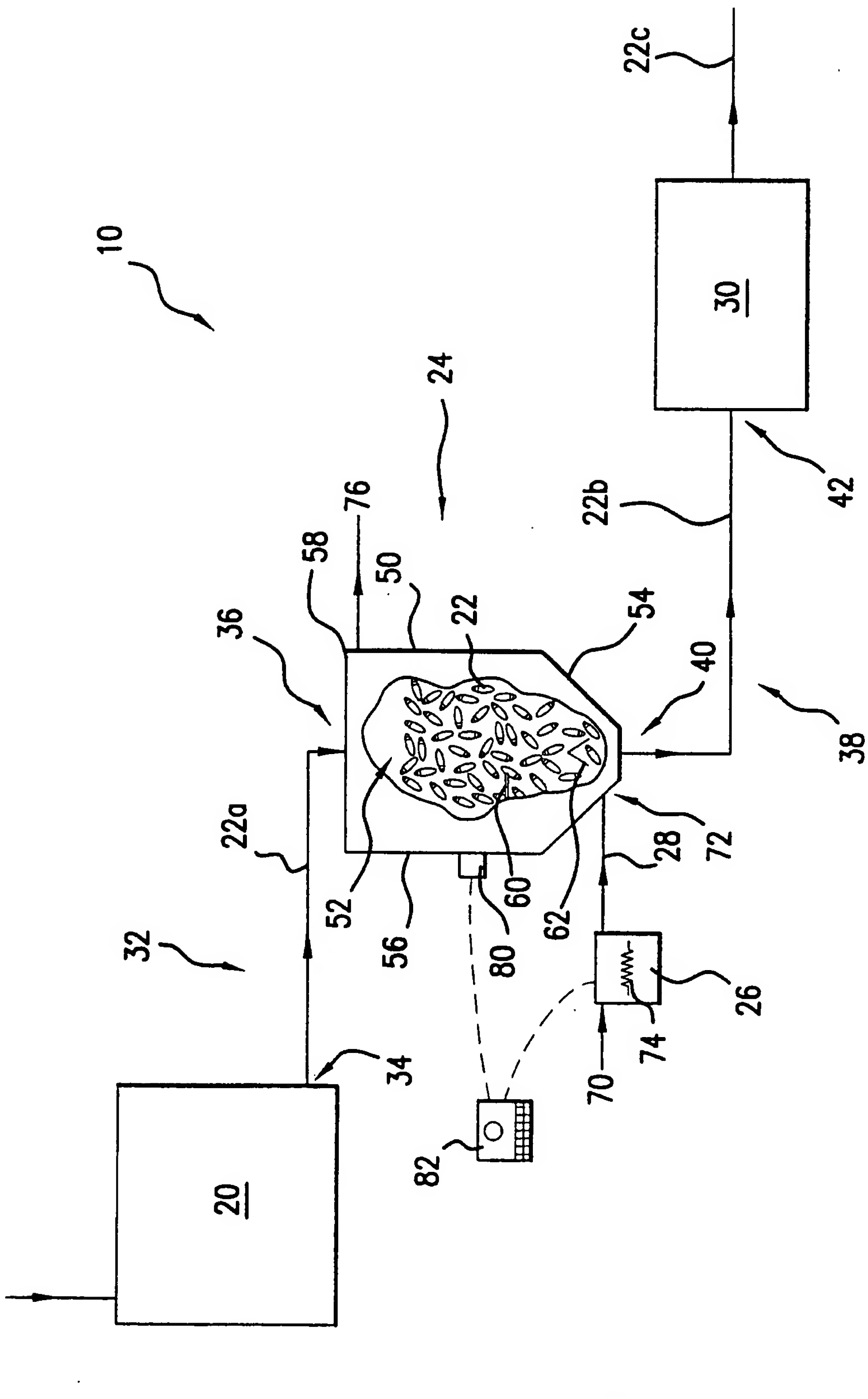
38. A method of crystallizing at least a finish portion of a PET container, comprising exposing at least a finish portion of an amorphous container preform to a gas comprising water vapor for a period of between about fifteen minutes to about six hours, and exposing at least the finish portion of the preform to energy until crystallized.

39. An apparatus for the production of heat set containers, comprising a hopper disposed in line between an injection molding machine and a crystallizing machine, said hopper comprising means for circulating warm, moist air.

40. The apparatus of Claim 39, wherein said hopper has a size sufficient to give a residence time from about fifteen minutes to about six hours.

41. A method for the production of heat set containers, comprising forming a preform, contacting said preform with a gas comprising water vapor, and crystallizing at least a portion of said preform.

42. The method of Claim 41, wherein the step of contacting said preform with a gas comprising water vapor comprises exposing the preform to warm, moist air having a temperature of about 50°C for about one to four hours.


10
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22a
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72
74
76
80
82

FIG. 1

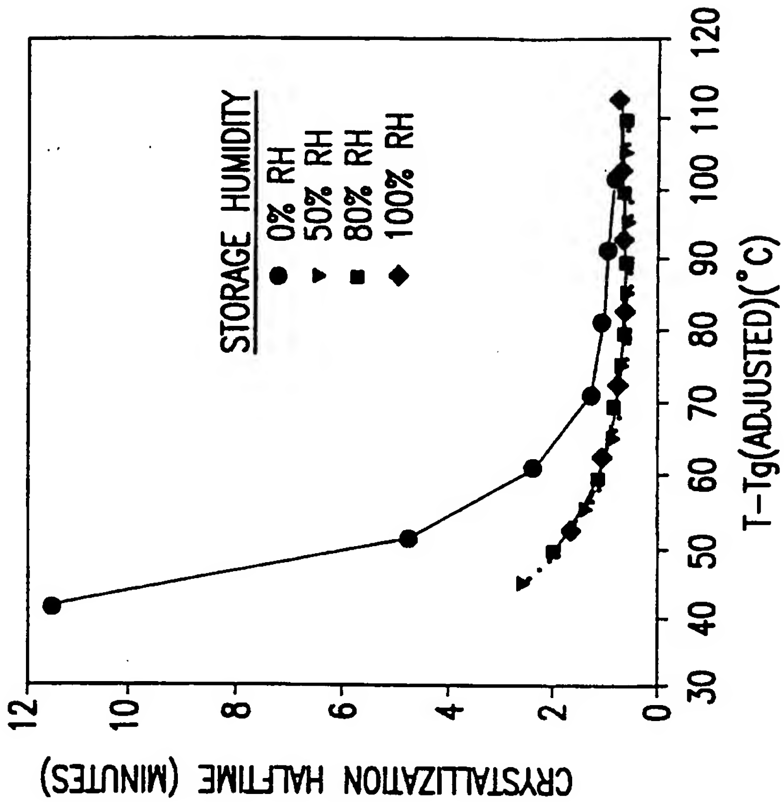

STORAGE HUMIDITY
0% RH
50% RH
80% RH
100% RH
CRYSTALLIZATION HALFTIME (MINUTES)
0 2 4 6 8 10 12
T−Tg(ADJUSTED)(°C)
30 40 50 60 70 80 90 100 110 120

FIG.3

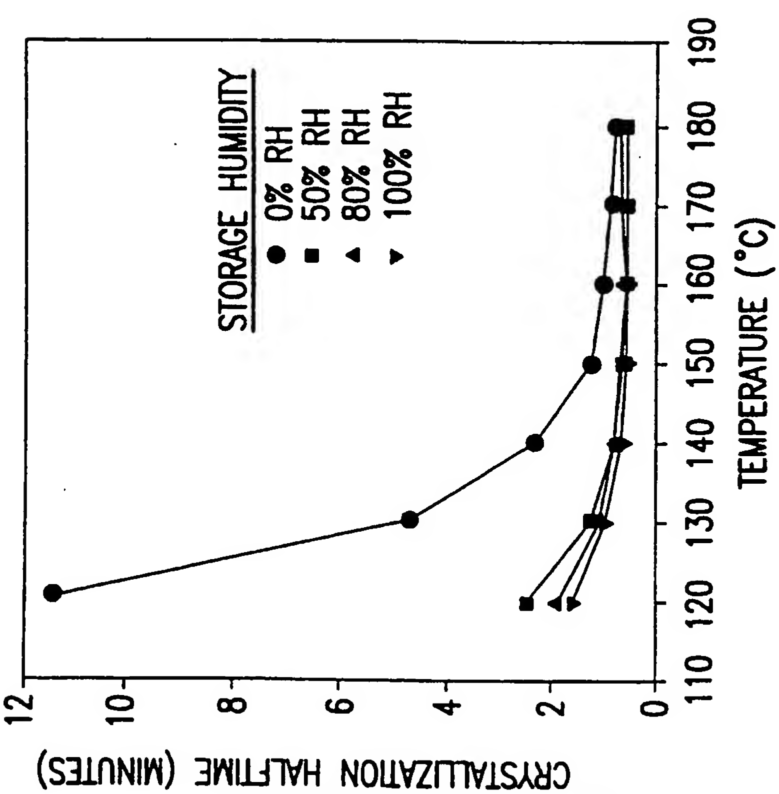

STORAGE HUMIDITY
0% RH
50% RH
80% RH
100% RH
CRYSTALLIZATION HALFTIME (MINUTES)
0 2 4 6 8 10 12
TEMPERATURE (°C)
110 120 130 140 150 160 170 180 190

FIG.2

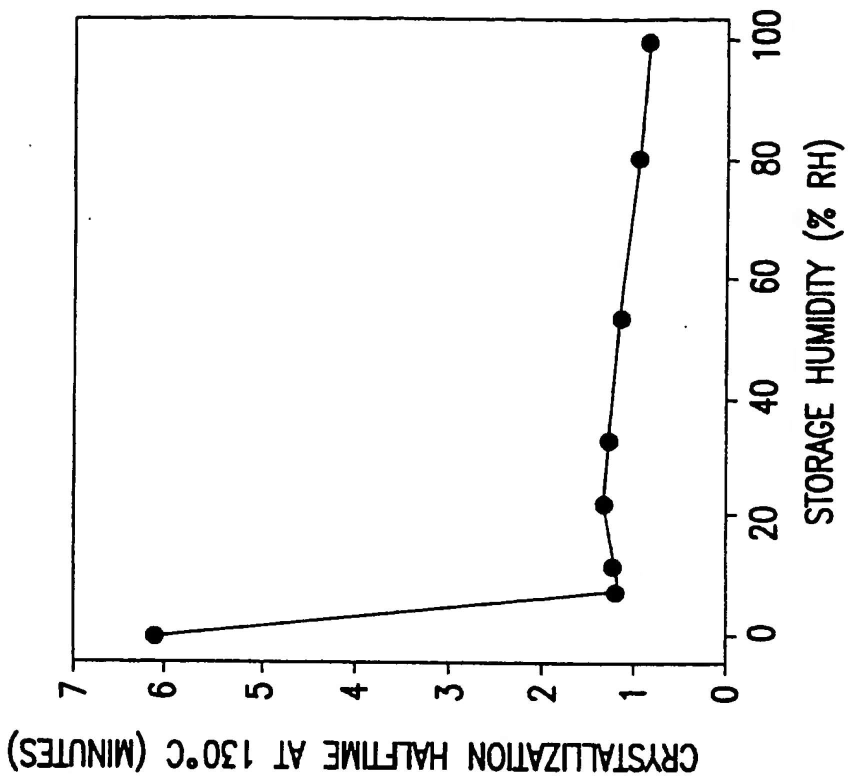

CRYSTALLIZATION HALFTIME AT 130°C (MINUTES)
STORAGE HUMIDITY (% RH)
0
1
2
3
4
5
6
7
0
20
40
60
80
100

FIG.5

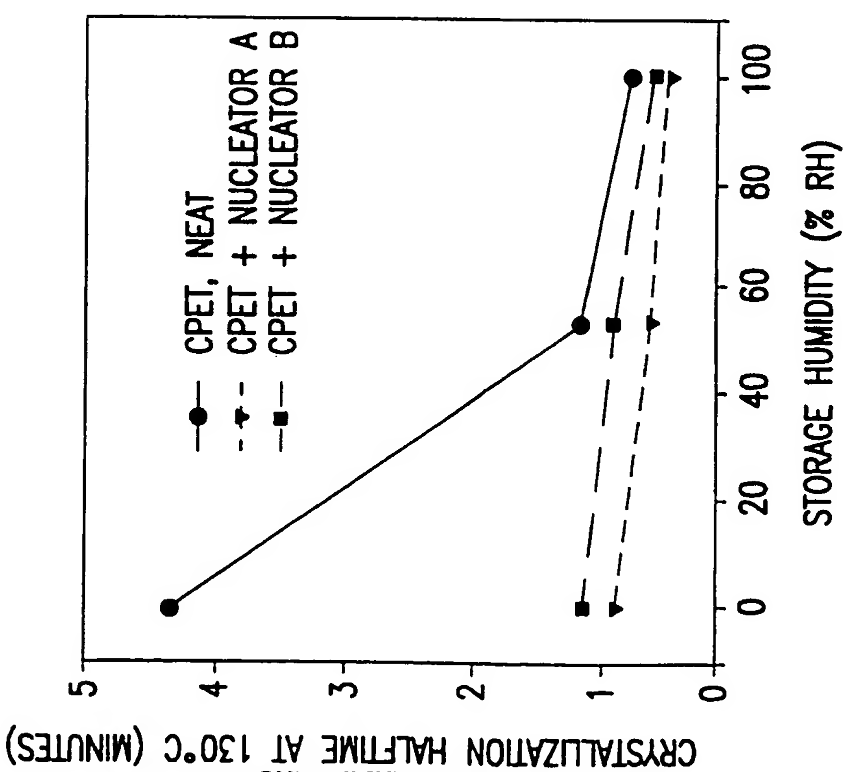

CPET, NEAT
CPET + NUCLEATOR A
CPET + NUCLEATOR B
CRYSTALLIZATION HALFTIME AT 130°C (MINUTES)
STORAGE HUMIDITY (% RH)
0
1
2
3
4
5
0
20
40
60
80
100

FIG.4

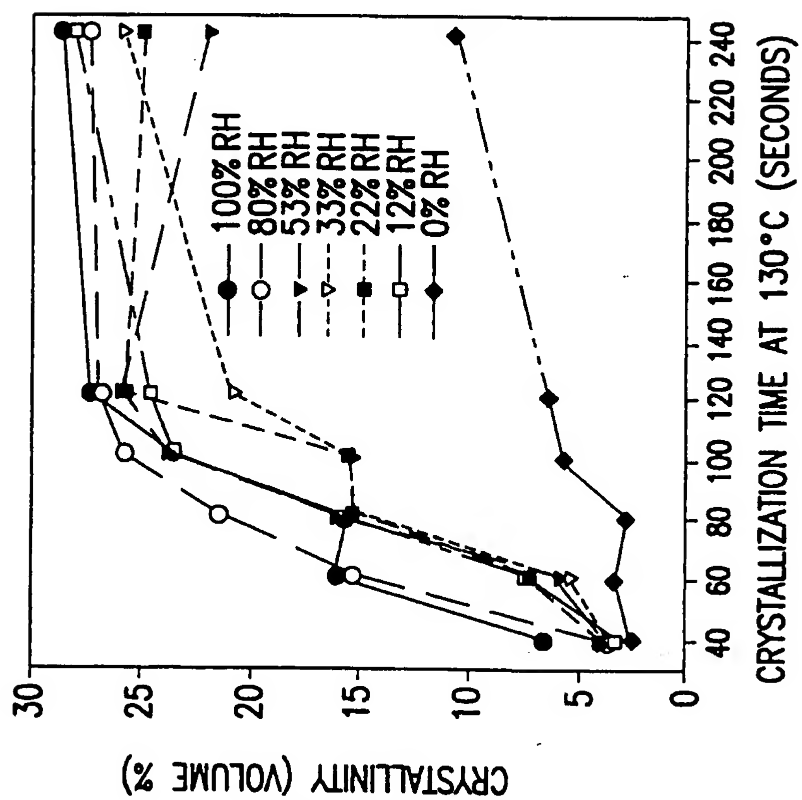

CRYSTALLINITY (VOLUME %)
30
25
20
15
10
5
0
40 60 80 100 120 140 160 180 200 220 240
CRYSTALLIZATION TIME AT 130°C (SECONDS)
100% RH
80% RH
53% RH
33% RH
22% RH
12% RH
0% RH

FIG.6

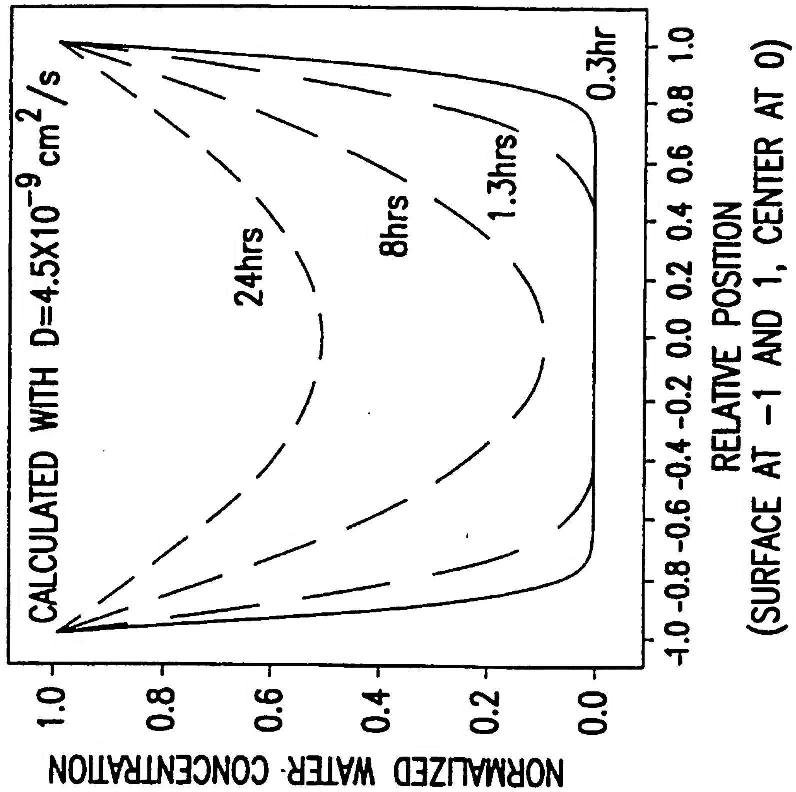
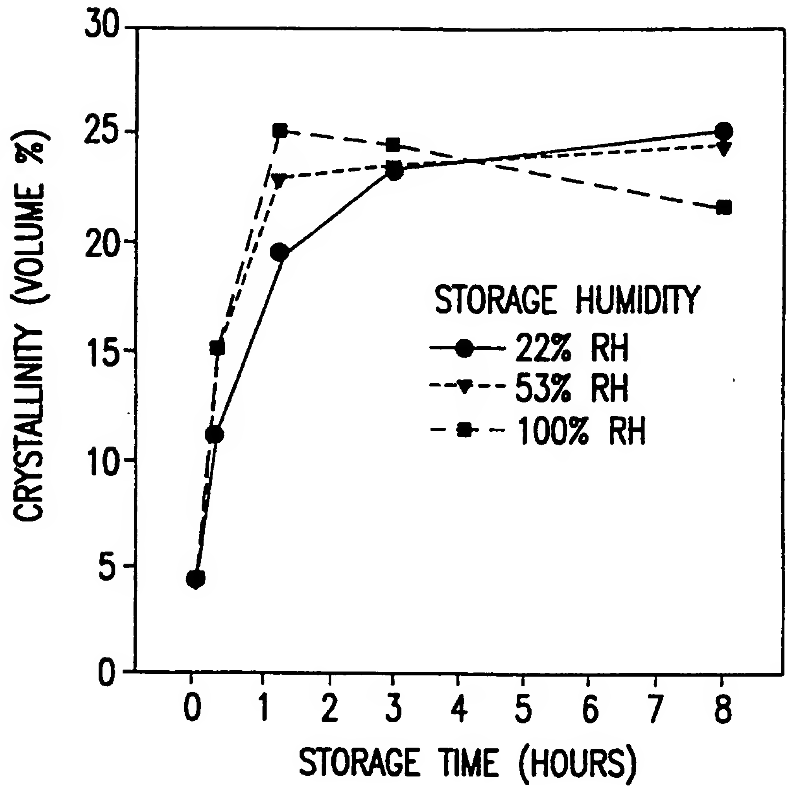

CALCULATED WITH D=4.5X10$^{-9}$ cm$^2$/s
NORMALIZED WATER CONCENTRATION
1.0
0.8
0.6
0.4
0.2
0.0
-1.0 -0.8 -0.6 -0.4 -0.2 0.0 0.2 0.4 0.6 0.8 1.0
RELATIVE POSITION
(SURFACE AT -1 AND 1, CENTER AT 0)
24hrs
8hrs
1.3hrs
0.3hr

FIG.7



30
25
20
15
10
5
0
CRYSTALLINITY (VOLUME %)
0 1 2 3 4 5 6 7 8
STORAGE TIME (HOURS)
STORAGE HUMIDITY
22% RH
53% RH
100% RH


FIG.8

# INTERNATIONAL SEARCH REPORT

Inte. onal Application No
PCT/US 99/11658

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 B29C49/42 B29C49/64

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
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| A | US 3 716 606 A (BAZETT P) 13 February 1973 (1973-02-13)<br>claim 1; figure 1<br>--- | 1-42 |
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| | -/-- | |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 September 1999 | 24/09/1999 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Dupuis, J-L |

2

Inte onal Application No
PCT/US 99/11658

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
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2

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Information on patent family members

International Application No
PCT/US 99/11658

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| | | SE 445100 B | 02-06-1986 |
| | | SE 7901198 A | 14-08-1979 |
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